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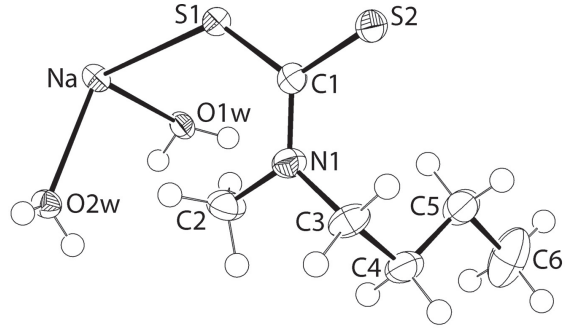
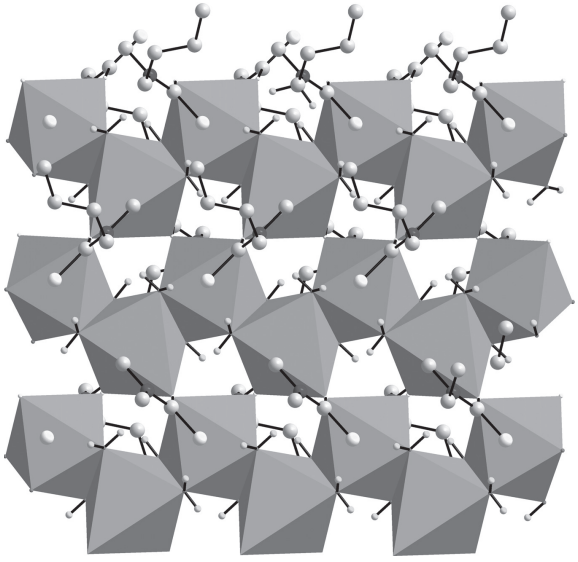
Crystal structure of *catena*-{di-*aqua*-sodium [*n*-butyl(methyl)carbamothioyl]sulfanide}$_n$, $[C_6H_{16}NNaO_2S_2]_n$





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Abstract

$[C_6H_{16}NNaO_2S_2]_n$, monoclinic, $P2_1/c$ (no. 14), $a = 16.3469(2)$ Å, $b = 5.7512(1)$ Å, $c = 11.8647(1)$ Å, $\beta = 91.046(1)°$, $V = 1115.27(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0212$, $wR_{ref}(F^2) = 0.0562$, $T = 100(2)$ K.

CCDC no.: 1948410

The constituents of the asymmetric unit are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.12 × 0.07 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	4.45 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13832, 1984, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1843
$N(param)_{refined}$:	143
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a Meltemp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained using a Perkin-Elmer RX1 spectrophotometer in a Nujol mull between KBr plates from 4000 to 400 cm^{-1}. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at room temperature in DMSO-d$_6$ solution on a Bruker AVN FT-NMR spectrometer with chemical shifts relative to tetramethylsilane.

The dithiocarbamate ligand was prepared in situ (acetone) from the reaction of CS_2 (Merck, 0.25 mmol) with *N*-butylmethylamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% *w/v*); CS_2 was added dropwise into the methanol solution

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.59781(2)	0.52552(5)	0.76260(2)	0.01336(10)
S2	0.73416(2)	0.72896(6)	0.90450(3)	0.01792(10)
N1	0.75278(7)	0.3872(2)	0.75606(9)	0.0178(2)
C1	0.70073(8)	0.5354(2)	0.80349(10)	0.0139(3)
C2	0.72612(9)	0.2217(3)	0.66871(12)	0.0233(3)
H2A	0.6870	0.1118	0.7006	0.035*
H2B	0.7736	0.1364	0.6411	0.035*
H2C	0.6999	0.3062	0.6061	0.035*
C3[a]	0.83995(8)	0.3713(3)	0.78991(12)	0.0225(3)
H3A[a]	0.8530	0.2092	0.8119	0.027*
H3B[a]	0.8504	0.4721	0.8562	0.027*
C4[a]	0.89498(14)	0.4450(6)	0.6948(2)	0.0233(7)
H4A[a]	0.8812	0.3534	0.6264	0.028*
H4B[a]	0.9527	0.4119	0.7161	0.028*
C5[a]	0.88555(14)	0.7022(4)	0.6689(2)	0.0249(7)
H5A[a]	0.9021	0.7957	0.7355	0.030*
H5B[a]	0.8277	0.7380	0.6498	0.030*
C6[a]	0.94223(11)	0.7645(4)	0.56471(16)	0.0443(5)
H6A[a]	0.9993	0.7273	0.5840	0.066*
H6B[a]	0.9375	0.9308	0.5477	0.066*
H6C[a]	0.9247	0.6738	0.4987	0.066*
C3′[b]	0.83995(8)	0.3713(3)	0.78991(12)	0.0225(3)
H3′1[b]	0.8617	0.2181	0.7670	0.027*
H3′2[b]	0.8450	0.3826	0.8730	0.027*
C4′[b]	0.8937(2)	0.5748(10)	0.7333(4)	0.0207(11)
H4′1[b]	0.8702	0.7280	0.7527	0.025*
H4′2[b]	0.9503	0.5686	0.7641	0.025*
C5′[b]	0.8950(2)	0.5485(7)	0.6061(3)	0.0231(12)
H5′1[b]	0.8388	0.5457	0.5739	0.028*
H5′2[b]	0.9235	0.4035	0.5846	0.028*
C6′[b]	0.94223(11)	0.7645(4)	0.56471(16)	0.0443(5)
H6′1[b]	0.9210	0.9041	0.6015	0.066*
H6′2[b]	0.9351	0.7794	0.4828	0.066*
H6′3[b]	1.0005	0.7471	0.5836	0.066*
Na	0.51573(3)	0.25752(8)	0.58118(4)	0.01467(13)
O1W	0.57908(6)	0.42617(16)	0.42368(7)	0.0164(2)
H1W	0.6222(7)	0.505(2)	0.4176(13)	0.025*
H2W	0.5809(9)	0.318(2)	0.3755(12)	0.025*
O2W	0.57935(5)	−0.10146(16)	0.55969(7)	0.0157(2)
H3W	0.6227(7)	−0.116(3)	0.5240(11)	0.024*
H4W	0.5840(9)	−0.191(3)	0.6157(10)	0.024*

[a]Occupancy: 0.631(5), [b]Occupancy: 0.369(5).

(10 mL). The resulting mixture solution was kept at 273 K for 1 h. The filtrate was evaporated until a beige precipitate was obtained. The precipitate was recrystallized from acetone-methanol by slow evaporation to yield colourless crystals. Yield: 0.029 g (52.4%). **M.pt:** 333 – 334 K. **IR** (cm^{-1}) 1478 (s) ν(C—N), 1012 (s) ν(C—S), 955 (m) ν(C—S). **^{1}H NMR** (DMSO-d_6, ppm): δ 0.90 (s, 3H, CH_3), 1.20–1.49 (m, 4H, CH_2CH_2), 3.15–3.21 (m, 4H, water-OH), 3.25 (s, 3H, NCH_3), 3.90–4.00 (m, 2H, NCH_2). **^{13}C{^{1}H} NMR** (DMSO-d_6, ppm): δ 13.9 (CH_3), 20.1, 29.0 (CH_2CH_2), 42.6 (NCH_3), 57.1 (NCH_2), 199.5 (CS_2).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.98–0.99 Å) and refined as riding with U_{iso}(H) = 1.2–1.5U_{eq}(C). The O-bound H-atoms were located in a difference Fourier map but were refined with a distance restraint O—H = 0.84 ± 0.01 Å, and with U_{iso}(H) set to 1.5U_{equiv}(O). The C4 and C5 atoms of the *n*-butyl chain were found to be disordered over two positions. Refinement (independent anisotropic displacement parameters for all atoms) showed the major component has a site occupancy factor = 0.631(5).

Comment

The title sodium salt of *n*-Bu(Me)NCS_2^-, isolated as a di-hydrate, was determined as part of on-going systematic studies of dithiocarbamates, e.g. ester [5], salt [6] and zinc-triad compounds [7, 8]. The pivotal motivation for such systematic studies of dithiocarbamate-containing species is the quest to discover new structural motifs as realised in two recent studies, whereby novel one-dimensional coordination polymers with distinctive topologies have been revealed for cadmium dithiocabamate derivatives, namely linear $\{Cd[S_2CN(CH_2CH_2)_2O]_2\}_n$ [9] and twisted $\{Cd[S_2CN(iPr)CH_2CH_2OH]_2\}_n$ [10].

The asymmetric unit of the title salt hydrate is shown in the upper view of the figure (70% displacement ellipsoids; both images show only the major component of the disordered —CH_2CH_2— residue) and comprises a sodium cation, a *n*-Bu(Me)NCS_2^- anion and two water molecules of crystallisation. The NCS_2 chromophore is strictly planar (r.m.s. deviation = 0.0035 Å) with the Na [0.2527(9) Å], C2 [0.019(2) Å] and C3 [−0.083(2) Å] atoms lying to either side of the plane. There is a discrepancy in the C—S1, S2 bond lengths [C1—S1 = 1.7434(13) Å and C1—S2 = 1.7178(13) Å] consistent with some localisation of π-electron in the C1—S2 bond. The relative short C1—N1 bond length of 1.3357(17) Å is consistent with a significant contribution of the *n*-Bu(Me)N^+ = CS_2^{2-} canonical form to the overall electronic structure of the dithiocarbamate anion. The distinctive nature of the C—S bonds is reflected in the pattern of bond angles subtended at the quaternary-C1 atom. Thus, the angles involving the S2 atom are systematically wider than the angle not involving this atom [S1—C1—S2 = 120.55(7)°, S2—C1—N1 = 120.69(10)° and S1—C1—N1 = 118.75(10)°]. This contrasts the observation of a recently reported dithiocarbamate salt with an ammonium counter-cation wherein the angles subtended at the quaternary-C1 atom were in the narrow range 119.45(8) to 120.57(10)° [6]. The sodium cation is coordinated

by four water molecules as each of the independent water molecules is bidentate bridging [range of Na—O(water): bond lengths: Na—O2w = 2.3278(10) Å to Na—O2w^{i} = 2.4331(10) Å for symmetry operation (i) 1 − x, −y, 1 − z]. The distorted octahedral cis-O_4S_2 geometry is completed by two S1 atoms [Na—S1 = 2.9502(6) Å and Na—S1 = 2.9641(6) Å for (ii) 1 − x, −1/2 + y, 3/2 − z]. The participation of the S1 atom in two interactions with the sodium cation accounts for the relative lengthening of the C1—S1 bond with respect to the C1—S2 bond (see above). As seen in the lower view of the figure, a two-dimensional layer results from zig-zag chains of edge-shared octahedra linked to neighbouring rows *via* corner-shared octahedra. The layer assembles in the *bc*-plane and has a planar topology. Within this framework, water-O—H···S hydrogen bonds, involving both sulphur atoms, provide additional stability [O1w—H1w···S2^{iii}: H1w···S2^{iii} = 2.393(11) Å, O1w···S2^{iii} = 3.2301(10) Å with angle at H1w = 172.8(10)°; O1w—H2w···S1^{iv}: H2w···S1^{iv} = 2.406(12) Å, O1w···S1^{iv} = 3.2428(9) Å with angle at H1w = 170.5(12)°; O2w—H3w···S2^{iv}: H3w···S2^{iv} = 2.418(13) Å, O2w···S2^{iv} = 3.2407(9) Å with angle at H1w = 168.0(15)°; O2w—H4w···S1^{v}: H4w···S1^{v} = 2.394(15) Å, O2w···S1^{v} = 3.2346(9) Å with angle at H1w = 174.7(14)° for (iii) x, 3/2 − y, −1/2 + z, (iv) x, 1/2 − y, −1/2 + z and (v) x, −1 + y, z]. The layers stack along the *c*-axis direction being separated by hydrophobic interactions, much in the same way as reported recently in the structure of $Na_2[O_2CCH_2SC(=S)N(Me)n\text{-}Bu]_2{\cdot}3H_2O$ [11].

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References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of *N*-methyl-*N*-phenyl(methylsulfanyl) carbothioamide, $C_9H_{11}NS_2$. Z. Kristallogr. NCS **234** (2019) nrcs-2019-0511.
6. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of 4-phenylpiperazin-1-ium (4-phenylpiperazin-1-yl) carbothioylsulfanide, $[C_{10}H_{15}N_2][C_{11}H_{13}N_2S_2]$. Z. Kristallogr. NCS **234** (2019) nrcs-2019-0512.
7. Tiekink, E. R. T.: Exploring the topological landscape exhibited by binary zinc-triad 1,1-dithiolates. Crystals **8** (2018) 292.
8. Tiekink, E. R. T.: Perplexing coordination behaviour of potentially bridging bipyridyl-type ligands in the coordination chemistry of zinc and cadmium 1,1-dithiolate compounds. Crystals **8** (2018) 18.
9. Ahmad, J.; How, F. N.-F.; Halim, S. N. A.; Jotani, M. M.; Lee, S. M.; Tiekink, E. R. T.: A new structural motif for cadmium dithiocarbamates: crystal structures and Hirshfeld surface analyses of homoleptic zinc and cadmium morpholine dithiocarbamates. Z. Kristallogr. – Cryst. Mater. **234** (2019) 341–349.
10. Tan, Y. S.; Halim, S. N. A.; Tiekink, E. R. T.: Exploring the crystallization landscape of cadmium bis(*N*-hydroxyethyl, *N*-isopropyl-dithiocarbamate), $Cd[S_2CN(iPr)CH_2CH_2OH]_2$. Z. Kristallogr. **231** (2016) 113–126.
11. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of catena-{[tri-aqua-di-sodium bis(2-{[*n*-butyl(methyl) carbamothioyl]sulfanyl}acetate])}$_n$, $[C_{16}H_{34}N_2Na_2O_7S_4]_n$ Z. Kristallogr. NCS **234** (2019) nrcs-2019-0513.